USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 325
DETERMINATION OF DISSOLVED GASES IN WATER

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TABLE OF CONTENTS

1 SCOPE AND APPLICABILITY

This SOP describes the procedures used to determine dissolved gases in water including methane, ethane, ethene, propane, and carbon dioxide. This procedure may be extended to determine other dissolved gases in water. The applicability of these procedures to specific project data quality objectives (DQOs) must be assessed on a case-by-case basis.

This SOP is based on SOP RSK-175, *Sample Preparation and Calculation for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique*, Revision 0, August 1994. Deviations from reference method are described in Appendix A. Analytes and quantitation limits are provided in Appendix B.

2 METHOD SUMMARY

Headspace is created in a sample vial by displacing a portion of the water sample with helium. The sample vial is then heated and agitated to allow equilibrium to be reached for both phases. An aliquot of the headspace is injected onto the GC with a thermal conductivity detector (TCD) and flame ionization detector (FID) in series.

A temperature program is used in the gas chromatograph to separate the analytes of interest followed by detection. The TCD is used to determine carbon dioxide while the hydrocarbons are determined with the FID. High concentrations of hydrocarbons may also be determined with the TCD.

The analytical system is calibrated by equating the response of analytes in the headspace of standards injected into water with the analyte concentrations in the water phase of samples. Samples are analyzed in the same way as standards. Analyte concentrations are calculated directly from analyte responses using average calibration factors.

3 DEFINITIONS

Analytical Sample - Any sample in which analytes are being determined, excluding standards, blanks, or QC reference samples.

Calibration Blank (CB) - A blank that is the same matrix as the calibration standards, but without the analytes. This is equivalent to a Method Blank or Instrument Blank (IB) for this method.

Continuing Instrument Calibration Verification (CCV) – A standard containing the analytes of interest that is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout the analysis sequence (after every ten samples and at the end of the analytical run).

Demonstration of Capability (DOC) – demonstrations performed to verify and document that Region 9 laboratory procedures are capable of meeting performance criteria as outlined in the methods or other guidance documents.

FID - Flame Ionization Detector.

Initial Calibration Standards (ICAL) – Standards used to calibrate the instrument response with respect to analyte concentration.

Laboratory Control Sample (LCS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is analyzed like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

LIMS - Laboratory Information Management System. The Element database.

Matrix Spike (MS) - An aliquot of an analytical sample to which known quantities of the method analytes are added. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations. The MS is also known as laboratory fortified matrix (LFM).

Matrix Spike Duplicate (MSD) – A duplicate aliquot of an analytical sample to which known quantities of the method analytes are added. The MSD is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results and to determine laboratory precision. The MSD is also known as laboratory fortified matrix duplicate (LFMD).

Method Blank (MB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. This is equivalent to a Calibration Blank or an Instrument Blank for this method. The MB is also known as laboratory reagent blank (LRB).

Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Quantitation Limit (QL) - The concentration at which confidence in the reported value requires no qualifying remarks. A standard is analyzed at the QL to verify the previously established calibration curve.

Quantitation Limit Standard (QLS) - A standard used to check the accuracy of the analysis at the quantitation limit. The QLS is prepared at the lowest level calibration standard. The QLS is also known as low level calibration verification sample (LCV).

Sample Delivery Group (SDG) - A group of twenty samples or less from a project that is sent to the laboratory for analysis.

Second Source Calibration Verification (SCV) - A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check the initial calibration. The SCV is also known as quality control sample (QCS).

Stock Standard Solution (SSS) - A concentrated standard containing the method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Storage Blank (SB) – An aliquot of reagent water stored with samples in the sample storage refrigerator. The storage blank indicates whether contamination may have occurred during sample storage.

Surrogate Analyte (SA) - A pure analyte which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in a known amount before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

TCD – Thermal conductivity detector.

Water Sample - For the purpose of this method, a sample taken from matrices classified as drinking, surface, ground, storm runoff water, or industrial or domestic wastewater.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation must be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Many parts of the GC and autosampler operate at temperatures high enough to cause serious burns. Allow heated zones to cool below 50°C before working on or around them.

Flame ionization detectors use hydrogen gas as fuel. If hydrogen flow is on and no column is connected to the detector inlet fitting, hydrogen gas can flow into the oven and create an explosion hazard. Detector fittings must either be capped or have a column connected at all times.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure produces the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Glass vials containing acidic aqueous waste (HCl)	Hazardous Waste	Corrosive
Acidic aqueous waste	Hazardous Waste	Corrosive

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

- Aqueous samples should be collected in either 40-mL VOA vials or 20-mL headspace vials sealed with butyl rubber-Teflon faced septa since Teflon-faced silicone septa are reported to be permeable to light hydrocarbon gases. The headspace sample vials must be sealed with magnetic crimp caps compatible with the Gerstel MultiPurposeSampler MPS 2. Samples for hydrocarbon determination should be preserved with hydrochloric acid (HCl) to pH ≤2.

- Samples for carbon dioxide (CO_2) analysis must not be preserved; separate vials must be collected for CO_2 analysis.

- Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. Three vials should be sufficient to meet these objectives.

5.2 Internal Chain-of-Custody

- The sample custodian delivers water samples to a sample refrigerator in Room 203 or other area where the samples will be analyzed.

- Verify sample IDs and dates and times of collection against the chain-of-custody form.

- Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to "active out" and the location to the appropriate room number. At the end of the day, return sample containers to the "Home" locations. Update the LIMS database using the "return to home location" feature and update container disposition to "available in". Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Preservation Verification

Check the pH of the sample with 0-14 range pH paper using an aliquot of the sample not used for GC analysis. Record sample pH in the LIMS Bench Sheet. Samples for carbon dioxide determination must not be acidified.

5.4 Sample Storage

Samples must be stored between >0 and $\leq$ 6 °C. Retain samples for 60 days after the final analytical report is sent to the data user.

Return excess sample to the sample refrigerator in Room 203.

5.5 Holding Time

Unpreserved water samples must be analyzed within 7 days of sampling; preserved water samples must be analyzed within 14 days of sampling.

6 INTERFERENCES

Chromatographic interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated

baselines in chromatograms, or by carryover when low concentration samples are analyzed after high concentration samples.

Methane occurs naturally in the atmosphere and is a common contaminant. Automobile exhaust contains high levels of target compounds.

Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and dichloromethane) through the septum seal into the sample during storage and handling.

Cross contamination can occur when a sample that does not contain, or contains low concentration of dissolved gases is transferred or analyzed immediately after a sample containing relatively high concentrations. The helium purging assembly and syringes used in the transfer must be cleaned after transferring a sample with relatively high dissolved gas concentrations. Instrument blanks should be analyzed to ensure that carryover is not occurring.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. Minor deviations may be made in specific apparatus and materials provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- Data Acquisition and Processing System - Able to control the GC and headspace sampler and to acquire, store, and process gas chromatographic data. The software must be able to calculate calibration factors and the concentrations of analytes in samples. Agilent Technologies EnviroQuant ChemStation software with Gerstel MASter plug-in and data acquisition computers (or equivalent).

- Gas chromatograph equipped with TCD and FID detectors in series and a split/splitless injection port (Agilent 6890N gas chromatograph, or equivalent).

- Gas Chromatography Column – PLOT, packed, or micropacked column (or equivalent). A 1 m X 0.75mm ID Shin Carbon ST 100/120 micropacked column (Restek catalog number 19810-810) was used for the DOC of this method. Any column that provides adequate resolution, capacity, accuracy, and precision for the analytes of interest may be used.

- Headspace sampler and injector – Able to heat, agitate and inject headspace samples (Gerstel Multipurpose Sampler MPS 2, or equivalent).

- Helium purging assembly consisting of a 22-gauge Luer tip metal-hub needle fixed to a Teflon Luer lock syringe valve attached to a 500-µL gas-tight syringe barrel. A length of Teflon tubing that fits snugly in the syringe is connected to a helium supply at about 5 psig.

7.2 Reagents

All reagents, except for water and instrument gases, must be entered into the Region 9 LIMS.

- Reagent Water: All references to water in this method refer to water in which method analytes or other interferences are at less than one-half the QL of the analytes of interest. The Region 9 laboratory organic-free deionized water is further purified by bubbling a contaminant-free inert gas, such as helium, through the water. The reagent water used must be at the same pH as the associated samples. Reagent water lots are not tracked in the Region 9 LIMS.

- Hydrochloric acid (1:1): Dilute reagent grade concentrated hydrochloric acid with an equal volume of reagent water.

7.3 Standards

All standards must be entered into the Region 9 LIMS.

Store gas standard cylinders at room temperature. The expiration date for stock gas standards is as given by the manufacturer. If no expiration date is given the expiration date is two years from the date of manufacture. Standards must be checked frequently for stability. Working standards expire after 48 hours.

The following standard composition and concentrations are recommended only; other mixtures and concentrations can be used as required by the project.

- Hydrocarbon Gas Stock Standard – methane, ethane, ethene, and acetylene in nitrogen (1 mole % each (nominal)) (Scotty mix 216 - Supelco catalog number 23437, or equivalent:

Analyte	Formula	MW	Density, µg/µL@STP	Scotty std, µg/µL
Methane	CH_4	16	0.7143	0.0071
Ethene	C_2H_4	28	1.2500	0.0125
Ethane	C_2H_6	30	1.3393	0.0134
Acetylene	C_2H_2	26	1.1607	0.0116

- Hydrocarbon Gas Primary Dilution Standard (PDS) – Inject 1.0 mL of the stock standard into a flat-bottom 20-mL (nominal) crimp-capped, septum-sealed headspace vial filled with helium. Measure the volume of a representative vial by first taring the vial, filling it to the top with DI water, then reweighing the vial. The table below assumes an actual volume of 21.5 mL:

Analyte	ng/µL
Methane	0.33
Ethene	0.58
Ethane	0.62
Acetylene	0.54

- Prepare hydrocarbon initial calibration (ICAL) standards by first creating headspace as described in Section 8.3.1.1 in a round-bottom 20-mL crimp-capped, septum-sealed vial filled with reagent water. The reagent water should be acidified to pH ≤2 with 1:1 hydrochloric acid, usually a drop or two will be sufficient. Inject the appropriate amount of PDS or stock standard into the water phase. The following standard concentrations are based on a 16.1-mL water sample. The level 2 standard is the lowest standard used for methane. Level 1 is the lowest standard for ethane and ethylene.

  CAUTION: Use exactly the same vials for preparing standards that are to be used for analyzing samples. The "20-mL" designation is a nominal measurement only; vials from different manufacturers may have different actual volumes. Determine actual volumes as above. The sample volume is the actual vial volume less 5.0 mL.

Methane			
Level	Stock Std, µL	PDS, µL	Conc., µg/L
1(Not Used)		30	0.6
2(QLS)		60	1.2
3		200	4.1
4(CCV)	30		13.3
5	100		44.4
6	250		110.9
7	500		221.8

Acetylene			
Level	Stock Std, µL	PDS, µL	Conc., µg/L
1(QLS)		30	1.0
2		60	2.0
3		200	6.7
4(CCV)	30		21.6
5	100		72.1

Acetylene			
6	250		180.2
7	500		360.5

Ethene			
Level	Stock Std, µL	PDS, µL	Conc., µg/L
1(QLS)		30	1.1
2		60	2.2
3		200	7.2
4(CCV)	30		23.3
5	100		77.6
6	250		194.1
7	500		388.2

Ethane			
Level	Stock Std, µL	PDS, µL	Conc., µg/L
1(QLS)		30	1.2
2		60	2.3
3		200	7.7
4(CCV)	30		25.0
5	100		83.2
6	250		208.0
7	500		415.9

- Hydrocarbon Gas SCV - methane, ethane, ethylene, acetylene in nitrogen, each at 1 mole % (nominal) - Matheson GMT 10402TC (Alltech M7035) or equivalent. Inject 100 µL of the Stock Standard into the water phase of a vial prepared as described in Section 8.3.1 in a round-bottom 20-mL crimp-capped, septum-sealed vial filled with reagent water.

- Carbon dioxide stock standard – 99.8% CO_2; Matheson GMT10055TC (Alltech M7006) or equivalent.

- Prepare carbon dioxide ICAL standards by first creating headspace as described in Section 8.3.1 in a round-bottom 20-mL crimp-capped, septum-sealed vial filled with reagent water. The reagent water must not be acidified. Inject the appropriate amount of stock standard into the water phase. Additionally, add 100 µL of the 1% (nominal) acetylene in helium surrogate to each standard. The following standard concentrations are based on a 16.1-mL water sample.

CO2		
Level	Stock Std, µL	Conc., µg/L
1(QLS)	25	3,044
2	50	6,088
3(CCV)	100	12,176
4	250	30,440
5	500	60,881

- CO_2 SCV – Scott 99.8% (nominal) bone-dry CO_2 – Supelco 23402 or equivalent.

- Propane stock standard – 99% (nominal); Matheson GMT10367TC (Alltech M7014) or equivalent.

- Propane primary dilution standards – PDS1: inject 200 µL (0.2 mL) of the propane stock standard into a flat-bottom 20-mL (nominal) crimp-capped, septum-sealed headspace vial filled with helium. This will yield a concentration of 18.1 ng/µL assuming an actual vial volume of 21.5 mL. PDS2: inject 500 µL (0.5 mL) of PDS1 into a flat-bottom 20-mL (nominal) headspace vial as above. This will yield a concentration of 0.4 ng/µL assuming an actual vial volume of 21.5 mL. Measure the volume of a representative vial by first taring the vial, filling it to the top with DI water, then reweighing the vial.

- Prepare propane initial calibration (ICAL) standards by first creating headspace as described in Section 8.3.1 in a round-bottom 20-mL crimp-capped, septum-sealed vial filled with reagent water. The reagent water should be acidified to pH $\leq$2 with 1:1 hydrochloric acid unless the samples are not preserved. Inject the appropriate amount of PDS1 or PDS2 standard into the water phase. The following standard concentrations are based on a 16.1-mL water sample.

Propane			
Level	PDS1, µL	PDS2, µL	Conc., µg/L
1(QLS)		40	1.0
2		200	5.2
3	20		22.5
4(CCV)	100		112.4
5	250		280.9
6	500		561.8

- Propane SCV – Scott C.P. grade, 99% (nominal) or equivalent.

- Surrogate Standard – 1mole % (nominal) acetylene in helium; Matheson GMT10303TC (Alltech G0413) or equivalent.

- Surrogate SCV – Use acetylene in hydrocarbon gas stock standard at 1 mole % (nominal).

7.4 Supplies

- Vial – 20-mL (22.5 X 75.5mm), flat top, round bottom – Gerstel GC 93640 06, Alltech 97188 or equivalent.
- Vial – 20-mL (22.5 X 75.5mm), flat top, flat bottom – Alltech 6636 or equivalent.
- Crimp caps (magnetic) with TFE/Butyl Liner for 20-mL vial, 8mm center – Alltech 95156 or equivalent or
- Crimp caps (magnetic) with TFE/Silicone Liner for 20-mL vial, 8mm center – Alltech 95139 or equivalent.
- Crimper for 20-mm crimp caps – Gerstel GC 93640 01, Wheaton 224303 or equivalent.
- Gas-tight syringes, Luer tip with removable needle – SGE or Hamilton 1700 series or equivalent – 100-µL, 250-µL, 500-µL, 1-mL, 5-mL, 10-mL, and 25-mL.
- Replacement plunger assemblies for Hamilton 100-µL, 250-µL, and 500-µL gas-tight syringes – Hamilton 1162-02, 1162-03, and 1169-01 respectively.
- Teflon body two-way syringe valve (Luer Lock) – Supelco 20926, Alltech 86580 or equivalent.
- Syringe, 5-mL, non-sterile, polypropylene, Luer tip – BD or equivalent
- Syringe adapter for MicroMAT™ -10 gas standard cylinders – Alltech 8048 or equivalent.
- Septa for MicroMAT™ -10 Syringe adapter – Alltech 75801 or equivalent.
- Syringe adapter for MicroMAT™ -14 gas standard cylinders – Alltech 8810, Supelco 609010 or equivalent.
- Septa for MicroMAT™ -14 Syringe adapter – Alltech 8812, Supelco 608010 or equivalent.
- Regulator and gauge for 14 Liter gas standard cylinders (CGA160 fitting) – Supelco 507911 or equivalent.

- Luer tip syringe needles, 2" length, metal hub, 22 gauge, point style 5 –Supelco 20803, Alltech 7729-07 or equivalent.

- Syringe needle for 2.5-mL headspace syringe – Gerstel part no. 009980-046-00

- Injection unit tension cord for Gerstel MPS2 sampler – Gerstel part no. 093632-027-00.

- Needle guide tension cord for Gerstel MPS2 sampler – Gerstel part no. 093632-028-00.

8 ANALYTICAL PROCEDURES

This section describes procedures to set up, calibrate, and analyze samples. Depending on the specific analytes to be analyzed, it may be necessary to analyze multiple sample batches according to the following procedures.

8.1 Instrument Operation

- Make a ChemStation combined data acquisition / data analysis method using the operating parameters provided in Appendix E for the GC and autosampler. Save the method as outlined in Appendix D (ChemStation File Naming Convention). Adjust instrument operating parameters as needed to meet project, method and SOP requirements, and good chromatographic practice.

- The hydrocarbon analytes and the surrogate are quantitated using the FID; carbon dioxide is quantitated using the TCD. High concentrations of the hydrocarbon analytes may be quantitated using the TCD if it is calibrated for these analytes. Normally, however, the TCD is not turned on while analyzing for hydrocarbon gases.

- The sensitivity of the method can be adjusted to suit project requirements by changing the GC inlet mode (split or splitless), the split ratio, the volume injected, or, for hydrocarbons, the detector used (FID or TCD). If the sensitivity of the analytical system is changed a new DOC may have to be performed. The EPA Chemistry Technical Director will determine on a case-by-case basis if the change requires a new DOC prior to implementation.

- Prior to analyzing calibration, QC, or field samples make a LIMS batch containing the samples to be analyzed and an empty LIMS sequence to obtain LIMS assigned IDs for the calibration and QC samples.

- Ensure that appropriate waste containers are present and properly labeled.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Perform an initial calibration according to Section 8.3 using a minimum of five calibration levels for each analyte to establish an external standard linear calibration using the average calibration factor. Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Analyze each of the initial calibration standards and an instrument blank as described in Section 8.3. The following table shows an example hydrocarbon initial calibration sequence:

Sequence	Sample Name
1	IB/MB
2	Level 1 (QLS)
3	Level 2 (QLS-CH4)
4	Level 3
5	Level 4 (CCV)
6	Level 5
7	Level 6
8	Level 7
9	SCV
10	IB/MB

- Spike the water with the appropriate amount of hydrocarbon or carbon dioxide primary dilution standard (prepared as described in Section 7.3) for the specific calibration level being analyzed.

- Update each level of the ChemStation ICAL method with the new target analyte responses. Update the retention times in the method using the CCV level.

- Print a ChemStation Response Factor Report. See Appendix C for QC limits.

- Print page 3 of the ChemStation ICAL for methane to show that the method was updated correctly.

- Print the ChemStation initial calibration compound list report to verify that the average calibration factor is used.

- Save the method as outlined in Appendix D (ChemStation File Naming Conventions).

- Import the data files into LIMS and prepare a LIMS calibration. See LIMS manual for detailed procedure.

- Prepare and analyze the appropriate SCV standard immediately after the initial calibration. Prepare an SCV standard at the CCV concentration as described in Section 7.3.

- Evaluate the SCV by entering the results in the SCV worksheet of the RSK 175.xls spreadsheet. Print the SCV report and include it in the data package. See Section 9.2.1 and Appendix C for QC frequency and limits.

- Prepare and analyze a hydrocarbon or carbon dioxide MB/IB as described in Section 8.3.

8.2.2 Continuing Calibration Verification

- Prepare and analyze hydrocarbon or carbon dioxide CCVs as described in Section 7.3.

- Generate a ChemStation "Evaluate Continuing Calibration Report"

- Prepare and analyze hydrocarbon or carbon dioxide IBs as described in Section 8.3.

- Refer to Section 9.2.2 for frequency, acceptance criteria, and corrective action requirements.

- Update the center of the retention time window in the ChemStation quantitation method for each analyte and the surrogate by using the absolute retention times from the calibration verification standards at the beginning of the analytical sequence.

8.3 Sample Analysis

Analyze samples in preserved or unpreserved batches, which typically correspond to hydrocarbon and carbon dioxide analyses respectively.

Check that the numbers on the vials coincide with the numbers on the chain of custody forms to ensure that the correct sample is being analyzed.

Note sample anomalies that may affect results, such as bubbles in the sample vial, in the LIMS bench sheet comment field and/or the LIMS work order MMO field.

8.3.1 Sample Preparation

Allow the samples to reach ambient room temperature before analysis.

NOTE: Hydrocarbon samples may be preserved with acid to $\leq$ pH 2; carbon dioxide samples must not preserved. The pH of the reagent water used for batch and instrument QC should be the same pH as the associated samples. However, if preserved and unpreseved samples are received for hydrocarbon determination; analyze unpreserved samples along with preserved samples.

8.3.1.1 Creating Headspace

1. If the samples have been received in a 20-mL headspace vial, verify that the sample vials are sealed with a magnetic crimp cap compatible with the Gerstel MPS 2 autosampler. If not, the samples must be transferred to suitable headspace vials.

   Create headspace in the 20-mL sample vial by first clamping the vial in the inverted position. Insert the needle of the helium purging assembly with the valve closed all the way through the septum of the sample vial; then insert a 22-gauge needle attached to a 5-mL polypropylene syringe just through the septum. Turn on the helium purging valve and slowly withdraw the barrel of the syringe until 5 mL of water has been withdrawn. Turn off the helium purging valve and remove the helium purging needle and the 5-mL syringe from the septum. Remove the vial from the clamp, turn upright, and relieve the pressure in the vial by momentarily insert a 22-gauge needle through the septum.

2. If the sample has been received in a VOA vial, prepare a 20-mL headspace vial labeled with the sample ID to receive the sample aliquot by first flushing the vial with helium before sealing it with a magnetic crimp cap.

3. Clamp the VOA sample vial in the inverted position; then insert the needle of the helium purging assembly with the valve closed all the way through the septum of the sample vial. Next, insert the 22-gauge needle of a 25-mL syringe just through the septum of the sample vial. Turn on the helium purging valve and slowly withdraw the barrel of the 25-mL syringe until about 20-mL of sample has been withdrawn. Turn off the helium purging valve then remove the 25-mL syringe from the VOA vial and

quickly insert it through the septum of the previously prepared labeled headspace vial.

4. Insert a 22-gauge needle just through the septum of the previously prepared 20-mL headspace vial to vent the pressure when adding the sample. Then slowly inject the sample aliquot into the headspace vial until the sample volume matches a previously prepared QC sample. Remove the 22-gauge venting needle as soon as sample transfer is complete.

5. Remove the helium purging needle from the sample vial and the VOA vial from the clamp. Clean the helium purging assembly by removing the Teflon tubing from the syringe body and wiping it dry; re-insert the tubing in the syringe barrel then open the valve for a few seconds.

6. Check the pH of the sample with 0 -14 range pH paper using the remaining sample aliquot in the 25-mL syringe. Record the pH in the comment field and the pH field of the LIMS bench sheet. Clean the 25-mL syringe with DI water between samples.

7. Prepare MS/MSD QC samples by first transferring an aliquot of sample into each of two prepared 20-mL headspace vials as described above then spike the water phase with 100 µL of the appropriate stock standard.

8. Prepare an LCS QC sample by first creating headspace in a 20-mL round-bottom headspace vial filled with reagent water of the same pH as the associated samples as above. Spike the water phase with 100 µL of the appropriate stock standard.

9. Prepare appropriate QLS samples by first creating headspace in a 20-mL round-bottom headspace vial filled with reagent water of the same pH as the associated samples as above. Spike one HC QLS with 30 µL of the HC PDS for ethane and ethylene; spike the other with 60 µL of the HC PDS for methane. Spike CO_2 QLS with 20 µL of the CO_2 PDS.

10. Prepare a MB by first creating headspace as above in a 20-mL round-bottom headspace vial filled with reagent water of the same pH as the associated samples as above. This is equivalent to an IB and a calibration blank.

11. Spike the water phase of all field samples, and instrument, storage, and method blanks with 100 µL of the 1% acetylene in helium surrogate. Do not spike QLS, LCS, or MS/MSD QC samples with the acetylene surrogate as the spiking mix already contains acetylene.

12. Place the sample vials in the autosampler tray.

8.3.1.2 Preparing Dilutions

Dilutions are made by analyzing a smaller volume of sample.

1. Calculate the required sample volume using the following equation:

$$\text{Volume (mL)} = \frac{\text{Target ug/L}}{\text{Result ug/L}} \times \text{Full volume}$$

Where:

Target µg/L = ICAL mid-point concentration of analyte
Result µg/L = Analyte result in sample
Full Volume =Normal volume analyzed (16.1 mL)

Enter this volume in the Initial (mL) field of the LIMS bench sheet and after the client sample name in the Misc Info field of the ChemStation sequence.

2. Prepare a headspace vial for sample dilution by first filling a 20-mL round-bottom headspace vial with reagent water of the same pH as the associated samples. Then create a headspace in the vial equal to the required dilution sample volume plus 5 mL as in 8.3.1.1 paragraph 1.

3. Withdraw an aliquot of sample as in 8.3.1.1 paragraph 3. If the required volume is greater than 1 mL, withdraw the required volume plus 1 or 2 mL; otherwise withdraw the required volume plus the needle volume. Remove the syringe from the VOA vial and quickly insert it through the septum of the previously prepared headspace vial.

4. Insert a 22-gauge needle just through the septum of the previously prepared 20-mL headspace vial to vent the pressure when adding the sample. Then quickly inject the sample aliquot into the headspace vial until the sample volume matches a previously prepared QC sample. Remove the 22-gauge venting needle as soon as sample transfer is complete.

5. Spike the water phase with 100 µL of the 1% acetylene in helium surrogate.

6. Clean the helium purging assembly and any syringes used to make sample dilutions.

8.3.2 Analytical Sequence

Set up a ChemStation data acquisition sequence containing all field and QC samples to be analyzed. Name the data file according to the file naming conventions in Appendix D. Specify the ChemStation data acquisition method in the method column. Enter the laboratory sample ID or LIMS batch or sequence ID in the sample name field. Enter the client sample ID and sample volume used, if different from full sample volume, in the Misc Info field.

Include all QC sample extracts. See Section 9.3 for batch quality control (QC) frequency and corrective action requirements. It is highly recommended that the MB, LCS, and MS/MSD extracts be analyzed as early as possible in the analysis of a batch.

Save the ChemStation sequence as outlined in Appendix D (ChemStation File Naming Conventions).

The following table is an example hydrocarbon field sample analysis sequence:

Sequence	Sample Name	Sequence	Sample Name
1,2	Priming	9	MS Sample
3	IB	10	MS
4	CCV	11	MSD
5	C2H4,C2H6 QLS	12	IB/SB
6	CH4QLS	16 - 30	Field Samples
7	LCS	31	IB
8	MB	32	CCV

8.3.3 Analyte Identification and Quantitation

- All target analytes and surrogates in the field and QC samples must fall within the established retention time windows.

- If the retention time does not fall within the retention time window, then take corrective action to restore the system. If repairs to the system are required then a new initial calibration must be performed.

- Quantitate the sample data with the ChemStation data analysis method using the appropriate initial calibration. Print out quantitation reports and chromatograms for each field and QC sample.

- Populate the empty LIMS sequence with the samples actually analyzed by editing the empty LIMS sequence; import the sample information using Data Tool.

- Copy sample data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.

- After making an empty upload file containing the samples analyzed in the LIMS batch or sequence, import and merge the data files using the LIMS Data Tool module. Load the resulting merged data file into the LIMS Data Entry/Review table. See LIMS manual for detailed procedure.

8.3.3.1 Calculations

- Target analyte concentrations in samples as shown on the ChemStation quantitation report are calculated as:

  Equation 1:

$$\text{Concentration (ug/L)} = \frac{Ax}{CF}$$

  Where:
  A_x = area response for analyte x
  CF = mean calibration factor from the initial calibration (area/ [µg/L])

  LIMS calculates the final sample concentration.

  Analyte concentration in a sample may be calculated as follows:

$$\text{Concentration (ug/L)} = \frac{Ax \times Vo}{CF \times Vi}$$

  Where:
  Ax and CF as above
  Vo = Full sample volume (16.1 mL)
  Vi = Volume of sample analyzed (mL)

8.3.3.2 Manual Integration

- Review the baseline drawn by the data system integrator to verify that it accurately reflects the area response of the sample components. If in the judgment of the analyst, it does not, then correct the integration

using the ChemStation QEDIT software module. Document any manual integrations following the procedure described in USEPA Region 9 SOP 835, *Chromatographic Integration Procedures*.

8.3.4 QC Review

See Appendix C for QC frequency and limits.

- Process and review the results for the IB, CCV, and QLS instrument QC samples. Print a ChemStation *Evaluate Continuing Calibration Report* using the appropriate settings to verify that the CCV results are within QC limits.

  Evaluate the QLS results by importing the epatemp.txt files into the RSK 175.xls spreadsheet. Print the spreadsheet QLS report and include it in the data package.

  See Section 9.2 for instrument QC requirements.

- Process and review the results for the MB and MS/MSD batch QC samples and verify that the results are within QC limits.

  Evaluate the LCS result using the ChemStation LCS custom report. Print the LCS report and include it in the data package.

  See Section 9.3 for Batch QC requirements.

- Determine if surrogate recoveries for field and QC samples are within QC limits. Report the surrogate recovery from the FID. See Section 9.4 for Sample QC requirements.

- Review all sample results to determine if any samples need to be re-analyzed at a dilution.

  If any target analyte exceeds the initial calibration range of the FID it may be quantitated from the TCD provided it is within the linear calibration range of the TCD.

  If any target analyte exceeds the initial calibration range of the instrument, dilute by using a smaller aliquot of the sample combined with reagent water to a total volume of 16.1 mL and re-analyze. See Section 8.3.1.2.

- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

- Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook.

The following sections describe possible causes and corrective actions for common problems. Refer to Appendix F for routine preventative maintenance procedures and schedule.

8.4.1 Autosampler Maintenance

Symptom:

- Loss of sensitivity

  Possible causes: Clogged syringe, dirty syringe, vacuum created in sample vial, or improperly crimped sample vial.
  Corrective action: Clean syringe, use new sample, check vial cap by attempting to rotate by hand; if cap is loose crimping tool may need adjustment.

- Carryover

  Possible cause: Dirty syringe, clogged syringe.
  Corrective action: Clean syringe.

- Methane in blanks, high methane recovery in QLS.

  Possible cause: bent syringe needle.
  Corrective action: Replace MPS2 tension cords then replace needle.

8.4.2 GC Maintenance

Symptom

- Carryover

Possible causes: Analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.

Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.

  Possible cause: column flow rate problem.
  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.

  Possible causes: column flow rate problem, injection port leak, or column contamination.

  Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If symptoms remain, replace the column.

- Loss of resolution.

  Possible causes: column flow rate problem, injection port leak, or column contamination.

  Corrective action: Check for leaks, replace septum, replace the liner, replace inlet seal, and clip the column (a few inches to a foot or more) from the injector end. If symptoms remain, replace the column.

- Increased noise, wandering baseline or change in sensitivity (TCD).

  Possible cause: contamination of detector from column bleed or dirty samples.

  Corrective action: Thermal cleaning of detector. See *Agilent 6890 Series Gas Chromatograph Operating Manual Volume 3 – Detectors* for procedure.

- Flame goes out or will not light (FID).

  Possible cause: Dirty jet

Corrective action: Clean or replace jet. See *Agilent 6890 Series Gas Chromatograph Operating Manual Volume 3 – Detectors* for procedure.

- Increased noise or spikes or change in sensitivity (FID).

  Possible causes: Dirty jet, contaminated collector or upper Teflon insulator.

  Corrective action: Clean or replace jet, collector, or upper Teflon insulator. See *Agilent 6890 Series Gas Chromatograph Operating Manual Volume 3 – Detectors* for procedure.

9 QUALITY CONTROL

9.1 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880.

9.1.1 Retention Time Windows

1. Establish retention time windows for the target analytes and the surrogate whenever a new GC column is installed or a new DOC is required on each chromatographic column and instrument. Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. See Appendix C for retention time window criteria.

2. Record the analyte retention times from the analysis of CCVs to three decimal places (e.g., 9.007) from CCVs analyzed at the beginning and end of three analytical sequences. Since analyte retention times, especially that of ethane, seem to be affected by the number of injections made, possibly from water retention on the analytical column, injections made only before samples are analyzed may result in retention time windows that are too narrow.

3. Calculate the mean and standard deviation of the six absolute retention times. If the standard deviation of the retention times for a target compound is less than 0.01 minutes then use a default standard deviation of 0.01 minutes.

4. The width of the retention time window is defined as ±3 times the standard deviation of the mean retention time. If the default standard deviation is employed, the width of the window will be ±0.03 minutes.

5. For samples run during the same shift as an initial calibration, use the retention time of each analyte and surrogate in the mid-point standard of the initial calibration as the center of the retention time window.

6. Document the RT window calculations in a spreadsheet and store them in the laboratory where the samples are analyzed.

9.2 Instrument QC

9.2.1 Initial Calibration

Demonstration and documentation of an acceptable initial calibration are required before any samples are analyzed

The GC system must be calibrated whenever corrective action changes instrument response (e.g., detector gas adjustment, column replacement, etc.) is performed or if the calibration verification criteria cannot be met.

Normally the hydrocarbon analytes and the surrogate are quantitated with the FID; carbon dioxide is quantitated using the TCD.

- The calibration factor (CF) is calculated by the data system using the following equation:

Equation 2:

$$CF = (A_x)/ (C_x)$$

Where
A_x = Area of analyte x
C_x = Concentration of the standard injected (µg/L)

- The percent relative standard deviation (%RSD) of the CF values for each analyte is calculated by the data system using the following equation:

  Equation 3:

  $$\%RSD = (SD/ CF_{avg}) \times 100$$

  Where:

  $$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - CF_{avg})^2}{n-1}}$$

  SD = Standard deviation
  CF_{avg} = Mean calibration factor from the initial calibration.
  CF_i = Calibration factor for a calibration level.

- Verify that the %RSD of the target analytes and the surrogate are within QC limits immediately after the initial calibration is finished. See Appendix C for QC limits.

- If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the failed one in the ICAL. If more than one standard fails, corrective action is required.

- Analyze an SCV sample immediately after each initial calibration. Calculate the calibration factor (CF) for the target analytes and the surrogate compound using Equation 2.

- Calculate the percent difference (%D) between the SCV CF and the initial calibration average CF for the target analytes and the surrogate using the following equation:

Equation 4:

$$\%D = \frac{CF_c - CF_{avg}}{CF_{avg}} \times 100$$

Where:
CF_c = SCV or CCV CF
CF_{avg} = ICAL mean CF

- See Appendix C for QC limits. If the SCV sample fails it may be repeated once. If the second SCV fails, the cause for failure must be determined and corrected before analysis of samples can proceed.

9.2.2 Continuing Calibration Verification

- Analyze a CCV standard at the beginning and end of each analytical sequence.

- Calculate the calibration factor (CF) for the target analytes and the surrogate compound using Equation 2.

- Calculate the percent difference (%D) between the calibration verification CF and the initial calibration average CF for the target analytes and the surrogate using Equation 4.

- The %D must be within QC limits. See Appendix C for QC limits. If an analyte fails this criterion a second calibration verification may be analyzed. Repeated failure requires that corrective action be taken to restore the system before any additional samples are analyzed. All affected samples must be re-analyzed.

  If repairs to the system are required then a new initial calibration must be performed. The analyst should observe trends in the data such as declining response, erratic response, etc., which may signal the need for instrument maintenance.

- Acceptable sample analyses must be bracketed by the analyses of calibration verification standards that meet QC limits.

9.2.3 Quantitation Limit Standard

- Analyze a QLS for the analytes of interest each day when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit. Calculate the concentration of the target analytes using Equation 1.

- Calculate the percent of true value (Tv) for the target analytes using the following equation:

  Equation 5:

  $$\% \text{ True Value} = (Cd/Tv) \times 100$$

  Where:
  Cd = Concentration determined by analysis
  Tv = True value of standard

- If the % Tv is not within the QC limits in Appendix C, analyze a second QLS sample. Repeated failure requires that the cause be determined and corrected before analysis of samples can begin. If repairs to the system are required then a new initial calibration must be performed.

9.3 Batch QC

9.3.1 Method Blank

- Prepare and analyze a method blank (MB) with each batch or every 20 samples, whichever is more frequent, to demonstrate that the entire analytical system, from sample preparation through GC analysis, is free of contamination.

- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- Corrective action - If the MB result exceeds QC limits prepare and analyze another MB. If the MB result still exceeds QC limits corrective action must be taken to restore the system before any samples are analyzed. The most likely cause is a bent syringe needle. See Section 8.4.1.

- If the surrogate recovery does not meet acceptance criteria, prepare and analyze another MB. If the surrogate recovery still does not meet acceptance criteria, corrective action must be taken to restore the system before any samples are analyzed.

9.3.2 Laboratory Control Sample

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. An LCS is prepared and analyzed once per batch or every 20 samples, whichever is more frequent. The LCS is an MB spiked with matrix spiking solution.

- Calculate the percent recovery (%R) using the following equation:

  Equation 6:

  $$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

- %R must be within the QC limits in Appendix C. If acceptable accuracy cannot be achieved, prepare and analyze another LCS. If the LCS result still exceeds QC limits the problem must be located and corrected prior to reporting any sample data and before additional samples are analyzed.

9.3.3 Matrix Spike/Matrix Spike Duplicate

- Matrix spike (MS) and matrix spike duplicate (MSD) samples are prepared and analyzed for each batch of twenty or fewer samples prepared as a group. Matrix QC samples are usually designated in the field. In the event that a sample was not designated as the matrix spike sample and adequate sample volume exists, the analyst will choose one representative sample from the SDG for QC analysis. Do not choose any obvious field blanks as the QC sample.

- Calculate the recovery of each analyte using Equation 6.

- Calculate the relative percent differences (RPD) of the recoveries of each analyte in the MS and MSD using the following equation:

Equation 7:

$$\frac{\qquad\qquad}{\qquad\qquad}$$

Where,

MSC = Measured concentration of analyte in MS
MSDC = Measured concentration of analyte in MSD

- See Appendix C for QC limits. The MS/MSD recovery limits are advisory limits only. If the limits are not met, no corrective action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if QC limits are not met.

- The table below lists the action to be taken based on the LCS and MS/MSD results:

QC ACCEPTANCE MATRIX	+ = PASS				– = FAIL			
CASE	1	2	3	4	5	6	7	8
LCS - % REC	+	+	+	+	–	–	–	–
MS/MSD -% REC	+	–	+	–	+	–	+	–
MS/MSD – RPD	+	+	–	–	+	+	–	–

Case 1: batch acceptable.
Case 2: batch acceptable; matrix effect confirmed.
Cases 3 & 4: batch is unsatisfactory. Investigate MS/MSD problem and document findings in report narrative.
Case 5: batch rejected. May have to re-analyze new aliquots of samples unless LCS problem is determined and documented.
Cases 6, 7, & 8: batch rejected. Re-analyze new aliquots of samples.

9.3.4 Storage Blank

- Every Monday morning, or the first workday of the week, when samples for dissolved gas analysis are likely to be received, fill a 20-mL headspace vial

sealed with butyl rubber-Teflon faced septum with reagent water and another vial with acidified reagent water and store them with the samples in the sample storage refrigerator in Room 203.

- Analyze a storage blank (SB) once every week while samples for dissolved gas analysis are being stored waiting for analysis. Analyze preserved or unpreserved SB depending on whether the stored samples are preserved or unpreserved. The storage blank indicates whether contamination may have occurred during sample storage.

- If samples for dissolved gas analysis have been stored in the refrigerator during the previous week, analyze the storage blank the following Monday, or on the first workday of that week. If samples for dissolved gas analysis have not been stored in the refrigerator during the previous week, discard the blanks.

- Evaluate the SB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- If the SB does not meet QC criteria all affected data must be qualified. See Appendix M of the Region 9 Laboratory Quality Assurance Plan.

9.4 Sample QC

9.4.1 Surrogate Recovery

- Evaluate the surrogate recovery in all field and QC samples immediately after analysis.

- The surrogate recovery must be within QC limits. See Appendix C for QC limits.

- Take the following steps if surrogate recovery is not within the limits:

  1. Ensure that there are no calculation errors, and check the system performance.
  2. Re-analyze the sample if a system performance problem or calculation error is not evident. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The extract may be diluted for re-analysis if examination of the chromatogram so indicates.
  3. If re-analysis of the sample does not solve the problem, another aliquot of the sample may have to be analyzed.

- Do not re-analyze undiluted samples with surrogate recovery outside the limits if a diluted analysis with acceptable surrogate recovery is being submitted.

- Do not re-analyze the MS/MSD samples, even if surrogate recovery is outside the limits.

- If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis.

- If the surrogate recovery of the re-analysis of the sample is within limits, then the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis.

- If the surrogate recovery of the re-analysis is outside limits, report the results from the first analysis and submit the data from both analyses.

9.5 Method Performance

Region 9 Laboratory performance data are not available for CO_2 or propane. LCS recovery data will be collected and summarized for these analytes in future revisions of this SOP as they become available.

The following table summarizes method performance for the period May 26, 2009 to May 27, 2011.

Method Performance

Analyte	Matrix	QC Type	Analyses, n	Mean Recovery, %	95% Confidence Interval (2σ)
Carbon Dioxide	Water	LCS		TBD	TBD
Methane	Water	LCS	11	100	82.8 – 117
Ethane	Water	LCS	11	107	89.2 – 125
Ethene	Water	LCS	11	108	91 – 125
Propane	Water	LCS		TBD	TBD
Acetylene	Water	Surrogate	76	110	80.8 - 138

TBD: To Be Determined

The following functional areas of the SOP may be significant sources of analytical error:

- Volume of headspace vial used in the preparation of the PDS and the ICAL standards must be known as accurately as possible as this will affect the concentration of the standards.

- Volume of headspace vial used for sample analysis must be known as accurately as possible as this will affect the volume of sample analyzed and the aqueous phase/headspace ratio.

- The volume of water and the ratio of water to headspace must be the same for standards and for field and QC samples in order to accurately quantitate target analytes in samples from the ICAL. Therefore, the vials used for preparing standards, instrument and batch QC, sample dilutions, and analyzing samples must have the same volume.

- The headspace vial crimp caps must seal; caps that do not seal will result in loss of sample. Check seal integrity by attempting to twist the cap; if you can twist the cap the seal is not adequate. Discard and use another vial.

- Measurement of sample volume, especially when preparing sample dilutions.

- Samples containing high concentrations of dissolved CO_2 will generate pressure in the headspace vial, shifting the equilibrium to the water phase and which may cause low determination of hydrocarbons from the headspace. Document this condition in the LIMS bench sheet and if surrogate fails also flag result with surrogate failure flag and a custom flag indicating reason for failure.

10 DOCUMENTATION

10.1 Standards

Record all standards (ICAL, SCV/CCV, QLS, and surrogate and matrix spiking mixes) in the Element database. Include a copy of each Analytical Standard Record associated with sample analysis in the data package.

10.2 Analytical Sequence and Calibration

Document the analytical sequence and calibration in the Element database.

10.3 Analytical Report and Data Package

Analytical result reports are produced using the Element database. The data package is produced from ChemStation quantitation reports, Element database reports, and manual log records. Appendix G provides the typical format for data package deliverables.

10.4 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control. Document all preventive or routine maintenance performed, as well as repairs or corrective or remedial actions in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*. Also, document major changes or upgrades to instrument hardware or software in the maintenance logbook.

10.5 SOP Distribution and Acknowledgement

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

11 REFERENCES

Agilent Technologies, *EnviroQuant ChemStation Users Guide*

Agilent Technologies, *Agilent 6890 Series Gas Chromatograph Operating Manual Volume 1 – General Information*

Agilent Technologies, *Agilent 6890 Series Gas Chromatograph Operating Manual Volume 2 – Inlets*

Agilent Technologies, *Agilent 6890 Series Gas Chromatograph Operating Manual Volume 3 – Detectors*

Gerstel MultiPurposeSampler MPS 2 Operation Manual

Gerstel MASter Software Operation Manual

U.S. Environmental Protection Agency, *Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003.*

U.S. Environmental Protection Agency, *SOP RSK-175, Sample Preparation and Calculation for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique, Revision 0, August 1994*

U.S. Environmental Protection Agency Region 1, *Technical Guidance for the Natural Attenuation Indicators: Methane, Ethane, and Ethene, Revision 1, February 21, 2002*

U.S. Environmental Protection Agency Region 9 SOP 110, *Sample Receiving and Login.*

U.S. Environmental Protection Agency Region 9 SOP 125, *Disposal Procedures for Unused Aqueous Environmental Samples*

U.S. Environmental Protection Agency Region 9 SOP 706, *Laboratory Waste Management Procedures*

U.S. Environmental Protection Agency Region 9 SOP 805, *Temperature Monitoring*

U.S. Environmental Protection Agency Region 9 SOP 820, *Laboratory Discrepancy and Corrective Action Reporting Procedures*

U.S. Environmental Protection Agency Region 9 SOP 835, *Chromatographic Integration Procedures*

U.S. Environmental Protection Agency Region 9 SOP 840, *Notebook Documentation and Control*

U.S. Environmental Protection Agency Region 9 Laboratory SOP 880, *Demonstration of Capability*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. SOP RSK-175 uses Henry's law to calculate the concentration of analytes in the aqueous phase from the concentration of analytes in the headspace. In this method, the analytical system is calibrated by equating the response of analytes in the headspace of standards injected into water with the analyte concentrations in the water phase. Analyte concentrations in water samples are then calculated directly from analyte responses in the headspace and their average calibration factor.

2. SOP RSK-175 does not specify an equilibration temperature. This SOP uses 40°C.

3. Retention time windows are calculated from the analysis of six, not three, injections of standards analyzed at the beginning and end of three analytical sequences. Since analyte retention times, especially that of ethane, seem to be affected by the number of injections made, possibly from water retention on the analytical column, injections made only before samples are analyzed may result in retention time windows that are too narrow.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

Analyte	Chemical Abstracts Registry Number	QL (µg/L)
Carbon dioxide	124-38-9	3044
Methane	74-82-8	1.2
Ethene	74-85-1	1.1
Ethane	74-84-0	1.2
Propane	74-98-6	Not Established
Acetylene (surrogate)	74-86-2	1.0

QL is based on a 16.1-mL sample with 5-mL headspace

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

QC MEASURE	FREQUENCY	CRITERIA
Initial Calibration (ICAL) RSD	After failure of CCV	≤ 20
Calibration Verification (CCV) %D	Beginning & end of each analytical sequence	≤ ±20
Second Source Calibration Verification (SCV) %D	After each ICAL	≤ ±30
Quantitation Limit Standard (QLS)	1/batch or 20 samples	± 40% of TV
Blanks – MB, IB	1/batch or 20 samples	< ½ QL
Storage Blank (SB)	Weekly, when analyzing samples	< ½ QL
Laboratory Control Sample (LCS) %R	1/batch or 20 samples	See table
MS/MSD %R	1/batch or 20 samples	See table
MS/MSD RPD	1/batch or 20 samples	See table
Surrogate Recovery of QC and field samples (except IB) %R	1/each field & QC sample	See table
Retention Time Windows	With DOC & annually	±0.03 minutes, or as determined

QC Limits

Analyte	LCS %R*	MS/MSD %R**	MS/MSD RPD**
Methane	70 – 130	70 - 130	20
Ethane	77 - 137	70 - 130	20
Ethene	78 - 138	70 - 130	20

*Limits are based on historical data from May 26, 2009 to May 27, 2011.
** Insufficient data for historical limits; values are laboratory defaults from the QA Plan.

LCS and MS/MSD recovery limits for CO_2 or propane cannot be calculated since laboratory performance data are not available. Recovery limits of 70 to 130 percent will be used until method performance results are available.

Surrogate % Recovery QC Limits (3σ)

Surrogate	%R
Acetylene	66.4 - 153

Surrogate %R is based on historical data from May 26, 2009 to May 27, 2011.

APPENDIX D.
CHEMSTATION FILE NAMING CONVENTIONS

ChemStation File Naming Convention

Data, Methods, and Sequences will be stored on the Chemstation computer as follows:

Directories:
On the Workstation
Whenever possible, the D drive should be used for storage
Data: D:\MSDCHEM\1\Data\MMDDYIAT or C:\MSDCHEM\1\Data\MMDDYIAT
Methods: D:\MSDCHEM\1\Methods or C:\MSDCHEM\1\Methods
Sequences: D:\MSDCHEM\1\Sequence or C:\MSDCHEM\1\Sequence

For system controlling multiple instruments, the instrument number, i.e. 1, may be changed to reflect the instrument number. Systems running older revisions, MSDCHEM is named HPCHEM

On the LAN:
Data: I:\DATA\Room Number\Instrument\Year\Data\MMDDYIAT
Methods: I:\DATA\Room Number\Instrument\Year\Methods
Sequences: I:\DATA\Room Number\Instrument\Year\Sequence

Methods:
MMDDYIATC

For systems limited to 8 characters file name:
MDDYIATC
Where M: Month 1-9, A-October, B-November, C-December

Sequence:
MMDDYIAT

Tune Files: (GC/MS)
MMDDYIA

Data Files
MMDDYIQnn

For systems limited to 8 characters file names:
MDDYIQnn
Where M: Month 1-9, A-October, B-November, C-December

Where:
MM: Month 01-12

DD: Day 01-31

Y: Year (i.e. 7 for 2007)

I: Instrument ID

GC:	6890-1	1
GC/MS:	5973L	L

A: Analysis, as follow:

504	E
Air	A
BFB	F
BNA	B
BN-Low	H
Congeners	C
DFTPP	T
P/P	P
PCBs	S
Acids-Low	O
RSK175	R
Soil Gas	A
TPH-G	G
TPH-D	D
VOA	V

T: Matrix Type (if applicable)

Water	W
Soil	S
Air	A
Medium-Level	M
Oil	O
Other	X

Q: QC type: (if applicable)

BFB	F
DFTPP	T
IC	I
Second Source	C
CV	C
LCV	C

C: Channel (if applicable)
A for front
B for back

nn: Sequential number 01, 02, 03, ...

APPENDIX E.
RECOMMENDED INSTRUMENT PARAMETERS

OVEN
Initial temp: 35 'C (On) Maximum temp: 320 'C
Initial time: 5.00 min Equilibration time: 0.50 min
Ramps:

#	Rate	Final temp	Final time
1	30.00	320	0.50
2	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 15.00 min

FRONT INLET (SPLIT/SPLITLESS)
Mode: Splitless
Initial temp: 125 'C (On)
Pressure: 50.00 psi (On)
Purge flow: 0.0 mL/min
Purge time: 0.50 min
Total flow: 20.1 mL/min
Gas saver: Off
Gas type: Helium

BACK INLET (UNKNOWN)

COLUMN 1
Packed Column
Model Number: Restek 21064
ShinCarbon ST
Max temperature: 330 'C
Mode: constant pressure
Pressure: 50.00 psi
Inlet: Front Inlet
Outlet: Back Detector
Outlet pressure: ambient

COLUMN 2
Packed Column
Inlet: (unspecified)
Outlet: Front Detector

FRONT DETECTOR (FID)
Temperature: 250 'C (On)
flow: 40.0 mL/min (On)
flow: 450.0 mL/min (On)
Mode: Constant makeup flow
flow: 20.0 mL/min (On)
Makeup Gas Type: Helium
Flame: On
Electrometer: On
Lit offset: 1.0

BACK DETECTOR (TCD)
Temperature: 250 'C (On)
Reference flow: 22.0 mL/min (On)
Mode: Constant makeup flow
Makeup flow: 4.0 mL/min (On)
Makeup Gas Type: Helium
Filament: Off
Negative polarity: Off

SIGNAL 1
Data rate: 5 Hz

SIGNAL 2
Data rate: 5 Hz

Type: front detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

Type: back detector
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
Derive from back detector

COLUMN COMP 2
Derive from front detector

THERMAL AUX 1
Use: Valve Box Heater
Description: S-IN OUT
Initial temp: 80 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

GERSTEL MPS Headspace Injection

SYRINGE SETTINGS

Syringe	:	2.5ml-HS
Syringe Temperature	:	40 'C
Flush Time	:	2.00 min

SAMPLE PREPARATIONS

Incubation Temperature	:	40 'C
Incubation Time	:	5.00 min
Agitator Speed	:	500 rpm
Agitator On Time	:	30 s
Agitator Off Time	:	2 s

SAMPLE PARAMETERS

Volume	:	600.0 uL
Fill Speed	:	50.00 uL/s
Pullup Delay	:	1.0 s
Fill Strokes	:	0
Inj. Speed	:	500.00 uL/s
Pre Inj. Delay	:	0.00 s
Post Inj. Delay	:	0.10 s
Inj. Penetration	:	25.00 mm

MULTIPLE HEADSPACE SAMPLE ENRICHMENT (MHSE) AND/OR PRESSURIZE

Pressurize	:	not used
MHSE Inj. per Run	:	1

CYCLE SETTINGS

Cycle Time	:	25.0 min

APPENDIX F.
PREVENTIVE MAINTENANCE REQUIREMENTS

Item	Frequency	Actions/Comments
Gas purifiers (carrier gas & detector gas)	Annually	Replacement schedule is based on capacity and grade of gases. In general, replace non-indicating traps every 6-12 months or when indicating traps start to change color.
Split vent trap	Annually	Replace.
Syringes and/or syringe needles	As needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	With each ICAL	Check. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Replace with liner or with signs of wear.
Inlet septum	Daily (when analyzing samples)	Check often. Replace after about 100 injections or when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As needed	Bake out when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.). Replace when baking out no longer restores chromatographic performance.
Ferrules	As needed	Replace ferrules when changing columns and inlet/detector parts.
FID Jet & Collector	As needed	Clean when deposits are present. Replace when they become scratched, bent, or damaged, or when having difficulty lighting or keeping flame lit.
TCD	As needed	Thermally clean by "baking-out" when a wandering baseline, increased noise, or a change in response is present. Replace when thermal cleaning does not resolve the problem.
Gas standard syringe adapter septa	As needed	Replace after about 100 penetrations or when there is little resistance to penetration.
Column	As needed	Decrease in acetylene response is a good indicator

APPENDIX G.
TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms
- EPA Review Form
- ESAT technical review guide
- Discrepancy Reports (if applicable)
- Work Order Memo (if applicable)
- Daily folder review forms or checklists
- Analysis matrix listing all analytical runs (for organics only)

Tracking Forms
- Work Order(s)
- COC(s)

Sample Preparation (for projects that require extraction or digestion)
- Bench Sheets (and extraction logs, where used)
- Sample cleanup data and records (e.g. GPC logs)
- Moisture data as applicable

[Analysis Method] Data (For each method where multiple methods in package)
- Bench sheet(s) where not used in Sample Preparation section
- Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:
- Initial Calibration Data
- Sample Data

Miscellaneous Data
- Other data as applicable (e.g. conductivity for perchlorate)

Standard Records
- Standards records from LIMS (and logbook pages as needed)

APPENDIX H.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 325
Revision: 2 , Effective: 6/20/2011

DETERMINATION OF DISSOLVED GASES IN WATER

Revision	Effective Date	Description
2	06/20/2011	1. Revised carbon dioxide calibration levels and QL. 2. Updated SOP format to current EPA Region 9 Laboratory requirements. 3. Corrected equation for RPD to absolute value. 4. Removed reference to Method 3810.